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Self-powered sensitive and stable UV-visible photodetector based on GdNiO₃/Nb-doped SrTiO₃ heterojunctions

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The properties of perovskite nickelates are very sensitive to their oxygen content, which allows us to tune their electronic structures by varying the oxygen partial pressure during film deposition. Under the optimized condition, we have obtained GdNiO₃ films that are sensitive to a wide spectrum of light. By combining the GdNiO₃ film with Nb-doped SrTiO₃ to form a heterojunction, we design a self-powered photodetector with high sensitivity toward light with a wavelength between 650 nm and 365 nm. Under 365 nm illumination (50 μ W/cm²), the device shows a responsivity of 0.23 A/W at 0 V bias, comparable to or even better than the ultraviolet photodetectors made of semiconductor materials such as GaN or ZnO. The photo-dark ratio can be close to 10³ when the power light density reaches 0.6 mW/cm². Moreover, the device performance is very stable without any decay after 6 months. *Published by AIP Publishing.*

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Photodetectors (PDs) are essential components for communication, environmental monitoring, optoelectronic circuits, and intelligent buildings.^{1–4} Commercial products based on GaN, Si, and InGaAs work well in ultraviolet (UV), visible, and near-infrared (Near-IR) subbands, respectively. For many practical applications, wide spectrum photo-detection is necessary. Therefore, it is desirable to develop a PD with high performance over a broad range of wavelengths. Many materials have been investigated for this purpose,^{5–10} such as CH₃NH₃PbI₃.¹⁰ However, the hybrid perovskites are not stable under ambient conditions and easily desolve in water, leading to serious environmental concerns. Recently, nickelates (RNiO₃, where R represents a rare earth lanthanide element) have attracted considerable interest due to the emergence of many exotic phenomena.^{11–15} For Sm and smaller rare earths, this system undergoes two transitions: from a paramagnetic metallic phase to a paramagnetic insulating phase, followed by an antiferromagnetic insulating phase at low temperatures. For bulk GdNiO₃ (GNO), the metal-insulator transition temperature T_{MI} is about 510 K and the Neel temperature T_N is about 180 K. Furthermore, one of the remarkable features of RNiO₃ is the dependence of their physical properties on the chosen rare earth element, which makes RNiO₃ a canonical example for bandwidth controlled metal-insulator transitions.¹⁶ These perovskite oxides are lead-free, are very

stable, and have tunable band gaps, ideal as light absorbing materials in optoelectronic devices.^{17–19} Moreover, RNiO₃ have shown *p*-type conduction at room temperature, making them good candidates for designing devices based on *p-n* junctions.

One of the key points in designing a PD is to establish an electric field to separate the photo-generated electron-hole pairs. This is usually achieved by applying an external bias to the light-absorbing material, and the photo-response can be adjusted by changing the bias. On the other hand, a passive operation can be achieved if the built-in electric field of a *p-n* junction is used for carrier separation. Here, we propose a self-powered PD based on a GdNiO₃/Nb-doped SrTiO₃ (GNO/NSTO) *p-n* heterojunction. A high responsivity of 0.23 A/W is demonstrated. It also shows a broadband response from 365 to 650 nm. A photo-dark ratio of >100 can be achieved under light (365 nm) of only 50 μ W/cm². Moreover, the device shows no change in performance after 6 months.

GNO thin films were grown on (001)-oriented 0.7 wt. % NSTO substrates by pulsed laser deposition. The laser pulse (248 nm) energy density was ~ 2 J/cm², and the repetition rate was 5 Hz. The substrates were heated to 725 °C during deposition. The film thickness was about 10 nm. After deposition, the samples were annealed *in situ* for 10 min and cooled down to room temperature. X-ray diffraction (XRD) measurement was conducted to identify the crystal structure using a Rigaku SmartLab instrument with Cu-radiation ($\lambda=1.5405$ Å). Ultraviolet photoelectron spectroscopy (UPS) measurements were performed in a home-built ultrahigh

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vacuum multi-chamber system with base pressure better than 1×10^{-9} Torr. The UPS source was a helium discharge lamp ($h\nu = 21.2$ eV). The photoelectrons were measured using an electron analyzer (Omicron EA125). X-ray absorption spectroscopy (XAS) measurements were performed at the photoemission station at the Beijing Synchrotron Radiation Facility of Institute of High Energy Physics, Chinese Academy of Sciences. The ultrahigh vacuum chamber background pressure is about 2×10^{-10} Torr. Spectroscopic ellipsometry measurements have been performed using a commercially available rotating analyzer instrument with a compensator (V-VASE; J.A. Woollam Co., Inc.) within the spectral range from 0.6 to 6 eV at the Singapore Synchrotron Light Source. Data have been collected at two incidence angles (50° and 70°). The optical bandgap E_g can be determined from the absorption coefficient α , calculated using the Tauc plot following $\alpha E = A(E - E_g)^n$, where α is the absorption coefficient, E is the photon energy, A is a constant, and n is equal to $1/2$ or 2 for direct- or indirect-gap materials, respectively. To collect light-generated carriers, square Au top electrodes with a diameter of $400 \mu\text{m}$ and a thickness of 6 nm were deposited on the GNO films through a metal shadow mask. All photo-response characteristics of the Au/GNO/NSTO photodetectors were measured using a pA meter/direct current (DC) voltage source (Hewlett Package 4140B) on a low noise probe station under dark and illuminated conditions. A UV (365 nm) light-emitting diode (LED) with adjustable light power density from 0.05 to 0.6 mW/cm^2 was utilized as the light source. Monochromatic laser diodes with four different wavelengths between 460 nm and 980 nm and an optical power density of 10 mW/cm^2 were also used as light sources. All these measurements were performed at room temperature.

The samples prepared under various oxygen pressures $P(\text{O}_2)$ of 300, 100, 20, 2, and 0.2 mTorr are named D1–D5, respectively. In bulk, GNO is orthorhombic with a room temperature pseudocubic lattice constant of $\sim 3.756 \text{ \AA}$,²⁰ which is smaller than that of STO ($a_{\text{STO}} \sim 3.905 \text{ \AA}$). Therefore, GNO will experience an in-plane tensile strain of 3.9% on STO. X-ray $\theta - 2\theta$ scans show only diffraction peaks from the substrates and GNO films (Fig. 1(a)), indicating the high quality films. The $(002)_{\text{pc}}$ diffraction peaks of the GNO films shift towards smaller diffraction angles with decreasing $P(\text{O}_2)$, and the calculated c -axis lattice constants are 3.84, 3.87, 3.92, 3.97, and $4.01 \text{ \AA}$ for samples D1, D2, D3, D4, and D5, respectively. We attribute the change in the lattice constant to the oxygen vacancies. In order to maintain the charge neutrality, Ni ions change from Ni^{3+} to Ni^{2+} upon the introduction of oxygen vacancies, leading to a larger Ni ionic radius and larger lattice constant.¹⁷ Similar effects have also been reported in other perovskite oxides.^{21,22}

To further understand the influence of oxygen vacancies on the Ni $3d$ –O $2p$ hybridization and Ni valance state, we turn to X-ray absorption spectroscopy (XAS) measurements. Figure 1(b) shows the Ni L_{32} edge spectra. The intensity ratio between the L_3 (around 853 eV) and L_2 (around 870 eV) peaks increases with decreasing $P(\text{O}_2)$, suggesting lower Ni valence in GNO films deposited under lower $P(\text{O}_2)$, consistent with the electron-doping effect of oxygen vacancies.^{23,24} The L_3 portion of the spectra reveals a sharp peak near 853 eV and a broad satellite peak near 854 eV, labeled as A and B, respectively. The clear split indicates that the samples are insulating.^{25,26} By comparing with the Cu L -edge spectra of cuprates,^{27,28} we suggest that the satellite peak B may be related to ligand holes formed due to the hybridization between Ni $3d$ and O $2p$ orbitals. Further evidence can be

FIG. 1. (a) XRD results for the five samples D1–D5. “S” denotes the diffraction peaks of the substrates. “F” denotes the diffraction peaks of GNO films, labeled as dashed lines. Ni L_{32} edge (b) and O K edge (c) spectra of three representative samples. (d) Measured absorption coefficient of the GNO films. The inset shows the Tauc plot results.

FIG. 2. (a) Device architecture of the Au/GdNiO₃/NSTO PDs. (b) Energy levels and work functions of the various components in the devices. The dashed lines denote the Fermi level (E_F). (c) Time-dependent photo-response of the PDs under alternating dark and illumination (365 nm UV light and 0.6 mW/cm²) conditions. (d) Calculated photo-dark ratio and R of the PDs as a function of $P(O_2)$.

found in the O K -edge absorption spectra (Fig. 1(c)). The intensity of the pre-peak near 529 eV (labeled by a red arrow) is a measure of the covalency in nickelates,²⁹ which decreases for samples deposited under low $P(O_2)$, indicating that the Ni $3d$ -O $2p$ hybridization strength decreases with decreasing $P(O_2)$.

In Fig. 1(d), we present the absorption coefficient α of the five samples, which are obtained from spectroscopic ellipsometry measurements. The corresponding optical bandgaps can be obtained from Tauc plots (the inset of Fig. 1(d)). Clearly, the GNO film deposited under lower $P(O_2)$ possesses larger optical bandgaps. This is consistent with the XAS results. As the Ni²⁺/Ni³⁺ ratio increases with decreasing $P(O_2)$, both valence and conduction bandwidths will be reduced due to the larger Ni²⁺ ionic radius/Ni-O bond length (d_{Ni-O}) and smaller Ni-O-Ni bond angle.³⁰ The smaller bandwidths further lead to stronger Coulomb repulsion among the electrons and induce a larger Mott-Hubbard splitting. Both effects contribute to the larger bandgap.¹⁷

Figure 2(a) shows schematically the self-powered PD based on the GNO/NSTO heterojunction. Semitransparent Au is used as the top electrode, which forms Ohmic contact with GNO. The built-in electric field at the GNO/NSTO interface provides the driving force for efficient separation of photo-generated carriers. Therefore, this device can operate

without an external power source. Figure 2(b) shows the energy diagrams across the heterojunctions. For NSTO, the Fermi level (E_F) is close to the conduction band minimum (CBM; $E_C \sim 4.0$ eV) due to the high doping concentration of 0.7 wt. %. The optical bandgap values of GNO films are extracted from the Tauc plots. The values of the valance band maximum (VBM) and work function of GNO films are obtained from ultraviolet photoelectron spectroscopy (UPS) measurements. The work function of the GNO film and the built-in electric field at the GNO/NSTO interface decrease with decreasing $P(O_2)$. The photo-response of the Au/GNO/NSTO PDs under alternating dark and illumination (365 nm UV light and 0.6 mW/cm²) conditions is shown in Fig. 2(c). The current increases upon illumination, stays roughly constant during illumination, and returns to the dark value when the UV light is turned off. To quantify the photo-responses of the devices, we define the photo-dark ratio as I_{ph}/I_{dark} , where I_{ph} ($I_{ph} = I_{light} - I_{dark}$), I_{dark} , and I_{light} are the photocurrent, the dark current, and the total current under illumination, respectively. The responsivity (R) is defined as $R = I_{ph}/(P_{in} \cdot S)$, where S is the effective contact area (1.6×10^{-3} cm²) and P_{in} is the power density of the light. Oxygen pressure dependences of the photo-dark ratio and R for the Au/GNO/NSTO PDs are shown in Fig. 2(d) and Table I. Sample D3 shows the best photo-response with a photo-dark ratio of

TABLE I. Performance of five different PD devices based on GNO/NSTO p - n heterojunctions. The light intensity of 365 nm UV light is 0.6 mW/cm².

Device	$P(O_2)$ (mTorr)	Optical bandgap (eV)	I_{dark} (nA)	I_{light} (nA)	Photo-dark ratio	R (mA/W)
D1	300	2.1	18.5	49.2	2.7	3.1
D2	100	2.3	3.14	28.8	9.2	2.7
D3	20	2.7	0.099	71.2	719.2	74.2
D4	2	2.97	0.051	9.37	183.7	9.7
D5	0.2	3.1	0.187	2.92	15.6	2.8

FIG. 3. (a) Time-dependent photo-response of the sample D3 measured using different wavelengths between 365 nm and 980 nm. (b) Calculated R of the sample D3 as a function of the illumination wavelength and the corresponding Tauc plot.

720 and R of ~ 74 mA/W, respectively. This is due to the combination of a large built-in electric field and low recombination of sample D3.

Our subsequent analysis focuses on sample D3. Figure 3(a) shows the photo-response measured using different wavelengths between 365 nm and 980 nm. The measurements were conducted under 0 V bias and a fixed light intensity of 10 mW/cm² except for 365 nm UV light (light intensity of 0.6 mW/cm²). It is observed that I_{light} is almost negligible under 808 and 980 nm light. A significant photo-response starts to appear when the light wavelength (λ) decreases to 650 nm. One of the key parameter for a PD is spectrum R , which matches the absorption result well as shown in Fig. 3(b).

We have also investigated the light intensity dependence of the photo-response at $\lambda = 365$ nm, as shown in Fig. 4. I_{ph} increases linearly with the light intensity as more electron-hole pairs are created. However, R decreases with increasing light intensity because of carrier trapping saturation and a reduction in the recombination barrier.³¹ The responsivity of the Au/GNO(20 mTorr)/NSTO PD is approximately 0.23 A/W at a light power density of 50 μ W/cm², comparable to or even better than the UV PDs made of semiconductor materials such as GaN (~ 0.01 A/W) or ZnO (~ 0.3 A/W).^{32–34} We have monitored the photo-response of the PDs for 6 months. Both I_{ph} and R are very stable without any decay over the whole period (Fig. 4(c)). Moreover, we have measured 10 randomly selected devices, and I_{ph} falls in the range of 10 – 20 nA (Fig. 4(d)), suggesting good reproducibility of the device.

In summary, we report a self-powered sensitive and stable PD based on the GNO/NSTO heterojunction. The device exhibits high sensitivity towards light between 650 nm and 365 nm. Under 365 nm illumination (50 μ W/cm²), the optimized device has a responsivity of 0.23 A/W at 0 V bias, and

FIG. 4. (a) Time-dependent photo-response of the sample D3 under illumination of the 365 nm UV light. Light intensity (mW/cm²) of each round of light illumination is labeled above each response peak. (b) I_{ph} and R as a function of light intensity. (c) Device stability in air recorded at 0 V bias. (d) Device reproducibility of our PDs.

the photo-dark ratio is close to 10^3 at a light intensity of 0.6 mW/cm^2 . The high photo-response primarily arises from the built-in field formed at the interface of *p*-GNO and *n*-NSTO. Our work extends the potential applications of nickelates.

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